



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Characterization of an Effective Cleaning Procedure for Aluminum Alloys: Surface Enhanced Raman Spectroscopy and Zeta Potential Analysis

N. J. Cherepy, T. H. Shen, A. P. Esposito, T. M. Tillotson

June 9, 2004

Journal of Colloid and Interface Science

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Characterization of an Effective Cleaning Procedure for Aluminum Alloys:
Surface Enhanced Raman Spectroscopy and Zeta Potential Analysis

Nerine J. Cherepy,* Tien H. Shen, Anthony P. Esposito and Thomas M. Tillotson

Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory,
Livermore, CA 94550

Article to be submitted to the
Journal of Colloid and Interface Science

*Corresponding author: MS L-091, Lawrence Livermore National Laboratory, Livermore, CA
94550, Phone: (925) 424-3492, Fax: (925) 423-8772, cherepy1@llnl.gov

ABSTRACT

We have developed a cleaning procedure for aluminum alloys for effective minimization of surface-adsorbed sub-micron particles and non-volatile residue. The procedure consists of a phosphoric acid etch followed by an alkaline detergent wash. To better understand the mechanism whereby this procedure reduces surface contaminants, we characterized the aluminum surface as a function of cleaning step using Surface Enhanced Raman Spectroscopy (SERS). SERS indicates that phosphoric acid etching re-establishes a surface oxide of different characteristics, including deposition of phosphate and increased hydration, while the subsequent alkaline detergent wash appears to remove the phosphate and modify the new surface oxide, possibly leading to a more compact surface oxide. We also studied the zeta potential of <5 micron pure aluminum and aluminum alloy 6061-T6 particles to determine how surface electrostatics may be affected during the cleaning process. The particles show a decrease in the magnitude of their zeta potential in the presence of detergent, and this effect is most pronounced for particles that have been etched with phosphoric acid. This reduction in magnitude of the surface attractive potential is in agreement with our observation that the phosphoric acid etch followed by detergent wash results in a decrease in surface-adsorbed sub-micron particulates.

Keywords: Aluminum surfaces, metal cleaning, Surface Enhanced Raman Spectroscopy, zeta potential.

1. INTRODUCTION

Aluminum and stainless alloys have been used extensively in the construction of the National Ignition Facility (NIF) – a 192-beam sports arena-sized laser facility at Lawrence Livermore National Laboratory. The parts and equipment exposed to the laser beam path must be kept very clean to protect laser optics from damage and prevent contamination of various coatings. The cleanliness requirements are similar to those achieved in the semiconductor industry. The NIF cleanliness criteria for any surfaces that are exposed to laser beam path are as follows:

1. Non-volatile residues (NVR) at less than Level A/10 ($< 0.1 \mu\text{g}/\text{cm}^2$),
2. Particulate contaminants at less than Level 83 (*i.e.* no more than 908 particles, $>5 \mu\text{m}$ in size, per square foot of flat surface) per MIL-STD-1246C specification [1].

To validate these cleanliness criteria, the NVR is measured by a) rinsing the metal surface with solvent, b) collecting the solvent/dissolved residue, c) evaporating the solvent, and d) weighing the residue. The particulate contaminant level is measured by the “particle swipe” test. This test uses white filter paper to swipe the metal surface and counts the numbers of collected particles under an optical microscope equipped with a fully automated counting system.

There are many large vacuum facilities requiring high-cleanliness conditions, such as particle accelerators. Literature concerning the cleaning procedures used for vacuum chamber construction materials describe the use of alkaline detergent washing followed by deionized water rinsing for aluminum alloys (see for example [2-5]). However to our knowledge, the use of a phosphoric acid etch prior to alkaline detergent washing has not been previously described as a standard cleaning protocol for aluminum vacuum chamber parts, nor has the problem of “smut” (loosely attached oxide and surface adsorbed particles) been addressed in this context.

In efforts to clean parts and equipment for the NIF, the parts made out of either cast or wrought aluminum alloys encountered great difficulty. These early experiences showed that even with several rigorous high pressure spray washes of alkaline detergent, the aluminum parts may pass the particle swipe test initially, but fail the test several days later in a Class 100 clean room. Close examination of the collected particles showed that most of the reappearing particles are metallic and micron-sized or smaller. Repetitive hand-wipes of the aluminum surface with a polar solvent, such as isopropyl alcohol, after the detergent wash helped to remove these sub-micron particles and eventually brought down the particle swipe value to below Level 83. However, considering the amount of equipment and parts that need to be cleaned, the hand-wiping after high pressure detergent wash certainly was not an economically acceptable cleaning procedure.

The chief remedy for particle contamination on aluminum surfaces has been the implementation of a phosphoric acid etching step prior to the detergent cleaning process [6]. This procedure has been clearly demonstrated on several alloys and parts to effectively minimize residual particles [7,8]. This multi-step cleaning process consists of a) an initial deionized water rinse, b) a 30 minute phosphoric acid etch, c) a second deionized water rinse, followed by d) a 5% Brulin™ 1990GD detergent high pressure spray wash, (or ultrasonic wash with Brulin™ 815GD for small parts) and e) final rinse with deionized water. The efficacy of the phosphoric acid etching may arise from: (1) its ability to dissolve small surface-adsorbed particles, (2) formation of phosphate and/or metaphosphate species at the surface, and (3) surface oxide modification, by conversion to a different predominant oxide structure and/or change in

morphology (e.g. surface area, compactness, etc.). Either (2) or (3) may modify the surface electrostatic attraction for residual particles [7].

We have postulated that when the aluminum parts are wet, surface adsorption of sub-micron particles is enabled via electrostatic attraction to the hydrated aluminum oxide surface [8]. We have observed that surface-adsorbed metallic particles are readily liberated by solvent wiping and that the removal of particles may be accelerated by drying with hot air. These two facts suggest a dehydration mechanism is responsible for the release of the strongly attached particles.

SEM micrographs of an AA6061-T6 aluminum surface before, versus after, the phosphoric acid etching are shown in Figure 1. Before the phosphoric acid etching, there are many sub-micron particles attached to the surface even after several rigorous high pressure detergent washes. The majority of these particles are aluminum particles; some α -eutectic inclusions (formed by impurities Fe, Si, etc.), iron oxides and stainless steel particles are also found. The origin of these particles is thought to arise from machining, caustic etching as well as contamination in the wash water during cleaning. As shown in Figure 1B, many of these particles disappeared after the phosphoric acid etch and detergent wash; the aluminum surface was also etched slightly by the acid. However, experimental results showed that the particle swipe value often increased right after the phosphoric acid etch [6] indicating that more debris were generated during the etching process. Fortunately, this debris could be easily washed away by the subsequent alkaline detergent cleaning process, and the reattachment of foreign metallic particles was prevented. Thus, the phosphoric acid not only dissolved the aluminum particles, but also in some way changed the nature of the aluminum surface, enabling a more effective washing step. For aluminum alloys, the effectiveness of the cleaning procedure has been

established in practice, but the mechanism whereby it removes surface-adsorbed particles is the subject of this work.

The native oxides of aluminum are expected to dominate the surface of most aluminum alloys, and to control the surface interactions. The passive layer is very thin, consisting of a ~1 nm barrier layer of Al_2O_3 at the aluminum surface and a porous, typically hydrated hydroxide/oxyhydroxide layer extending 5-10 nm. Corrosion of aluminum occurs at $\text{pH} < 4$ or $\text{pH} > 8.5$ according to the Pourbaix diagram [9], however the rate of corrosion can vary greatly depending on the identity of ionic species controlling pH. Phosphoric acid is second only to hydrofluoric acid in aggressivity in aluminum etching [10]. It is well known that acid etching removes and re-establishes the oxide layer, as well as selectively dissolving Mg_2Si precipitates present in AA6061. Moffitt and co-workers found using the elemental surface spectroscopy x-ray photoelectron spectroscopy (XPS) that while alkaline cleaning alone of AA2024 did result in diminished Mg at the surface, a nitric/hydrofluoric acid pickle treatment was more effective [11]. In general, the most effective cleaning procedures for Aluminum alloys are those that result in the thinnest, densest oxide, with the lowest amount of Mg, as the $\text{MgO-Al}_2\text{O}_3$ oxides tend to be thicker and more porous [2,11]. A thin oxide layer has less surface area, is less hydrated and is less able to adsorb particles.

The dehydration of aluminum oxide species has been studied by thermal gravimetric analysis [12]. Documented dehydration transitions (in air) include: (a) $\text{Al}(\text{OH})_3 \rightarrow \text{AlOOH}$ at 220-230 °C, (b) $\text{AlOOH} \rightarrow \chi\text{-Al}_2\text{O}_3$ at 310-325 °C, (c) $\text{AlOOH} \rightarrow \gamma\text{-Al}_2\text{O}_3$ at 450-525 °C. Some water seems to be present in samples up to 898 °C, finally desorbing completely by 1075 °C (shown via IR spectra/dehydration study, Rouquerol, et al. [13]). Under vacuum, the

dehydration of $\text{Al}(\text{OH})_3$ starts at 170 °C. However, the dehydration of aluminum hydroxide at room temperature, under vacuum over long periods of time, is not well understood.

In order to examine surface interactions resulting from the cleaning process on the aluminum surface, we used a variety of surface-sensitive techniques. In earlier work, we employed XPS to study the aluminum surface. The XPS result [7] suggested the presence of phosphate species on aluminum surface after a phosphoric acid etch.

We describe here the use of Surface Enhanced Raman Spectroscopy (SERS) to study the evolution of surface oxide at each cleaning step. SERS is a vibrational spectroscopic technique that is sensitive only to the surface. Its surface sensitivity derives from a very thin porous deposit of silver to enhance the Raman spectrum only of the surface it contacts [14]. Raman spectroscopy provides additional details regarding the molecular structure of the surface (not just the elemental composition) and it is nondestructive to the oxide structure. SERS allowed us to characterize the surface species as a function of surface preparation. The methodology for SERS applied to aluminum with chromium phosphate conversion coatings has been described by Ahern, et al., at Alcoa [15].

We also describe the use of zeta potential analysis to measure how the surface electrostatics are modified as a function of surface preparation and wash solution conditions. Swipe tests show high particle counts if surfaces undergo phosphoric acid etching only, or detergent wash only, but low residual particles counts when the phosphoric acid etch step precedes the detergent wash [6]. Zeta potential measurements can indicate whether the etch changes the surface electrostatics or changes the surface interactions with the detergent.

2. MATERIALS AND METHODS

2.1 Surface Species Identification.

Three coupons of Aluminum Alloy 6061 were prepared for SERS examination as follows:

1. Sample 1- machined surface wiped with acetone,
2. Sample 2- machined surface etched in phosphoric acid (30 vol% for 30 minutes, then rinsed in DI water,
3. Sample 3- machined surface etched in phosphoric acid (30 vol %) for 30 minutes, ultrasonic-cleaned with 3% Brulin™ 815GD (Brulin Corp., Indianapolis, IN) and 0.02% Zonyl™ (DuPont, Wilmington, DE) at 55°C for 20 min., followed by DI water rinse.

The sputter deposition of ~5 nm thick Ag coatings for the SERS measurements was conducted using planar magnetrons operated in the DC mode. When the base pressure of the vacuum chamber reached a value less than 0.0001 Pa, a sputter gas of Ar was flowed at a pressure of 0.65 Pa using a flow rate of 40 cc per min. The substrates were positioned 10 cm above the 6.3 cm diameter sputter target of 0.9999 pure Ag. The magnetron was operated with a forward power density of 0.15 Watts per cm sq. Each substrate was sequentially exposed to the shuttered deposition source 20 times over a total time period of 330 sec to yield an average deposition rate of ~0.015 nm per sec.

Excitation for Raman scattering was provided by the 488 nm line of an argon-ion laser (Lexel model 95). The laser beam was directed through a narrow bandpass filter to remove the residual laser plasma lines, and was then coupled into the entrance port of a Raman microscope (Jobin-Yvon T64000). A beamsplitter partially reflected the laser beam to a 20x objective lens (Nikon SLWD, NA 0.35) that focused the light to an 8-10 μm spot at the sample surface, and the

same objective lens was used to collect and collimate the Raman scattered light obtained at a 180° backscattering geometry. The incident laser power employed was 450 mW as measured at the sample with the objective lens removed.

The samples were placed on a motorized stage for positioning control, and were visually inspected using the optical microscope and video monitor, with the laser beam attenuated by a neutral density filter. Once a sample region was selected for analysis, the neutral density filter was removed and the scattered light was directed into the triple-grating spectrometer. The premonochromator was employed to remove the elastic scattering, and final dispersion of the scattered light was accomplished by a classically ruled 600 grooves/mm ($\lambda_{\text{blaze}} = 500 \text{ nm}$) grating. The dispersed light was detected with a liquid-nitrogen-cooled CCD camera (Jobin-Yvon Spectrum-1). Spectra were collected for 30 to 60 seconds, and were averaged ten times for a total integration time of 5-10 min for each sample region. All spectra were calibrated against a cyclohexane standard.

2.2 Surface Electrostatics Characterization.

Aluminum particles were obtained from Valimet (Stockton, CA). Two types of particles were studied, AA6061 (particle size 4-12 μm) and pure aluminum (average particle size 2 μm). They were studied as-received and suspended in solution by grinding for 1-2 minutes with mortar and pestle. To simulate phosphoric acid etching, particles were suspended in 30 vol% phosphoric acid for 5 minutes, then centrifuged, supernatant discarded, particles rinsed in DI water. Rinsing in DI water and centrifugation continued until pH registered neutral, usually 3 centrifugation cycles. After the final centrifugation cycle, particles were suspended in a solution of interest, either 5% Brulin™ 1990GD in DI water (pH =10.6), or plain DI water with pH

adjusted to 10.6 with sodium disilicate. The detergent composition of Brulin 1990GD is very similar to that of Brulin 815.

Zeta potential measurements were carried out using a Brookhaven Instruments ZetaPlus Analyzer. It uses electrophoretic light scattering and laser Doppler velocimetry to determine the zeta potential of particles suspended in solution. For all reported measurements at least 4 different samples were prepared and each was subjected to 20 light scattering measurements to generate enough data for statistical analysis.

3. RESULTS AND DISCUSSION

As shown in Figure 1, the phosphoric acid etching modified the AA6061 surface physically, minimized surface roughness and dissolved small surface-adsorbed particles. To determine whether phosphoric etching also changes the surface chemically, SERS was employed. We also probed the surface electrostatics using Zeta Potential Analysis to determine whether chemical modification of the surface resulted in changes in the strength of potential interactions between the surface and the particles.

3.1 Surface Species Identification.

SERS spectra were acquired using Raman microscopy, which provides the additional advantage of an optical image of the oxide deposits overlaid with spectral imaging for identification of the surface species. A photograph of Sample 3 is shown in Figure 2A, with the area where silver was deposited apparent as a dark film (porous and ~5 nm thick) over the central portion of the sample. A magnified optical image of this sample is shown in Figure 2B, showing machining grooves and pitting due to dissolution of Mg_2Si precipitates. Raman spectra were acquired of both the smooth areas and of the pitted areas. We attempted to obtain spectra from

regions of the aluminum without silver, but within the signal-to-noise of our measurement we could detect no Raman scattering.

We obtained SERS spectra of each sample in a “dark” or pitted region, as well in a smooth region. The spectra for a particular sample were similar, regardless of the surface characteristics (pitted or smooth), but the spectra of the pitted regions were much more intense, probably due to a thicker oxide in the pits. Figure 3 shows the spectra of Samples 1, 2 and 3. At least 4 different spectra for each sample and region type were acquired and found to be consistent with respect to spectral intensities. The spectra acquired in a pitted region and in a smooth area of Samples 2 and 3 were subtracted from the spectra acquired for Sample 1, and shown in Figures 4A and 4B, respectively.

Table 1 lists the vibrational modes of aluminum species that are known from the literature [15,16]. The SERS spectra of the three AA6061 samples show generally the same modes, with the exception of two modes at 965 and 1040 cm^{-1} , present in Samples 2 and 3. These modes are in good agreement with the frequencies typically exhibited by phosphate stretching modes as shown in Table 1. Ahern and co-workers assigned modes at 960 and 1055 cm^{-1} to aluminum phosphate [15]. Other studies point out that the vibrational frequencies of the isolated $[\text{PO}_4]^{3-}$ anion are at ~ 970 and ~ 1080 cm^{-1} , but these modes in AlPO_4 appear at higher frequencies, ~ 1069 - 1244 cm^{-1} [17]. This suggests that the phosphate modes detected via SERS correspond to very loosely bound, surface adsorbed phosphate. The intensity of these two modes is much greater for Sample 2, suggesting that the subsequent detergent wash is effective in removing the phosphate species from the surface.

The 1250-1700 cm^{-1} region shows more intensity for the phosphoric acid etched sample than for the other two samples. Primarily this is due to water molecules adsorbed on aluminum,

as assigned by Ahern, et al. This suggests that the phosphoric acid etch promotes hydration of the aluminum surface to form aluminum hydroxide in addition to excess surface adsorbed water. Ahern and co-workers also assign some of the intensity in this region to degraded organic materials (graphitic carbon) [15]. Indeed, some intensity appears to be lost in Sample 3 after the detergent wash, at ~ 1333 and 1580 cm^{-1} . Since both water and graphitic carbon have Raman modes in the same spectral region, this loss of intensity may be due to in part to removal of organics, but it seems unlikely that without an obvious contamination source that significant organics would be present on the freshly etched surface. Thus, the reduction in intensity in this region implies either surface dehydration or the removal of loosely attached hydroxide from the surface.

Relative to Sample 3, the spectrum of Sample 2 shows more intensity in the modes at 644 , 1163 , 1290 , 1452 , 1535 and 1600 cm^{-1} . Meanwhile, Sample 3 shows more intensity in modes at 772 , 815 , and 1388 cm^{-1} . Based on mode assignments as shown in Table 1, these differences indicate that Sample 2 contains relatively more octahedral aluminum (AlO_6) than tetrahedral aluminum (AlO_4) compared to Sample 3. This seems to indicate a different type of oxide is formed upon phosphoric acid etching, and that it is preferentially removed or transformed during the detergent wash step.

3.2 Surface Electrostatics Characterization.

We studied AA6061 and pure Al micron-sized particles in solution to try to understand how particles may adsorb at the surface via local attractive potentials. Surface-adsorbed aluminum particles, typically arising from machining debris of the bulk material, are negatively charged at the wash pH (~ 10.6), as is the bulk surface due to the hydroxide surface structure. These particles may interact electrostatically with the hydrated alumina surface via adsorbed cations.

The more negative the zeta potential of the particle and the surface, the greater the probability that strong attractive interactions may occur through the mediation of surface adsorbed cations. In addition, the more physically and chemically heterogeneous the surface, and the higher the hydroxide surface area, the greater the likelihood that local attractive potentials may form.

We measured the zeta potential for unetched particles of AA6061 and high purity Al in DI water (pH adjusted to 10.6 with sodium disilicate) and in 5% Brulin™ 1990GD. We performed the same measurements with particles that were surface etched with phosphoric acid. The results are shown in Table 2 and Figure 5. Unetched AA6061 particles show a decrease of about 20 mV in the “absolute magnitude” of the zeta potential in the presence of the detergent, from -72 to -51 mV. However, high purity Al particles did not exhibit a significant change in zeta potential in the presence of detergent. Etched particles show a larger decrease in the zeta potential magnitude with detergent. The magnitude of the zeta potential of both AA6061 and pure Al particles increases upon etching, and the magnitude of the zeta potential decreases in Brulin™ solution, for both types of particles. The magnitude of the zeta potential of etched AA6061 particles decreases in detergent solution, from -79 mV in pH-adjusted DI water to -42 mV in Brulin solution; a similar decrease is observed for etched pure Al particles, from -70 to -47 mV.

Our findings indicate that the phosphoric acid etching step results in multiple changes that may improve the ability of the detergent to adsorb or interact at the surface. They are:

1. A reduction in the amount of surface adsorbed metallic particles due to etching and dissolution of particles,
2. A physically smoother surface at the scale of the machining grooves,
3. Deposition of phosphate species at the surface,

4. Formation of different oxide species at the surface,
5. Increased relative hydration of the oxide at the surface.

Other chemical changes that we did not measure but have been observed in other studies of aluminum cleaning, such as selective removal of Mg from the surface [4,11] are also expected to alter the surface area and the surface electrostatics.

Brulin™ 1990GD, and Brulin™ 815GD are similar alkaline detergent formulations recommended for cleaning and degreasing metal parts. They are composed of a proprietary blend of anionic and non-ionic surfactants, along with some alkaline components and corrosion inhibitors. Cleaning of aluminum alloy 6xxx series has been found previously to be most effective with mildalkaline detergents, such as Almecco 18; surfaces cleaned with such detergents were found to have a thinner oxide, well depleted of Mg, compared to surfaces cleaned with strong alkaline detergents or solvents only [3]. Moffitt and co-workers found that an acid pickle was highly effective in removing Mg [11]. The effectiveness of our cleaning procedure in minimizing surface-adsorbed particles is likely due to (1) formation of a dense, thin barrier layer at the surface by the phosphoric acid etch, (2) detergent wash removing residual loosely attached oxide resulting from the acid etch, (3) relative dehydration of the surface during the detergent wash step, (4) removal of hydrated cations from the surface during the detergent wash.

4. SUMMARY

An effective cleaning procedure has been developed for aluminum alloys to minimize surface-adsorbed sub-micron particles and non-volatile residue. This procedure consists of a phosphoric acid etch followed by a wash with mild alkaline detergent. The SERS measurements indicate

that phosphoric acid etching chemically modifies the surface, depositing phosphate species, and resulting in an oxide layer with predominant octahedral alumina, as well as an overall higher degree of hydration. The subsequent alkaline detergent wash then removes phosphate, loosely attached surface oxide, and dehydrates the surface oxide layer, and leaves behind predominantly tetrahedral alumina. These changes are indicated by a decrease in the intensity of the phosphate modes at 965 and 1040 cm^{-1} and the Al-H₂O modes in the 1380-1610 cm^{-1} range, and a relative increase in the tetrahedral alumina modes at 772, 815, and 1388 cm^{-1} . The phosphoric acid etched AA6061-T6 particles exhibited a greater reduction in zeta potential (reduced from -79 mV to -42 mV) in the presence of alkaline detergent, compared to unetched AA6061-T6 particles (-72 mV to -51 mV). These measurements indicate that the newly etched surface appears to have a chemical and physical morphology that allows it to interact more strongly with the detergent, resulting in effective removal of surface-adsorbed water, cations, loosely-attached oxide, and inorganic surface-adsorbed particles.

ACKNOWLEDGEMENTS

We wish to thank William H. Gourdin of the NIF Non-Optical Materials Group for his support of this work. Thanks also to Alan Jankowski and Jeff Hayes for the silver deposition. We are grateful to Dan Farber for the use of his Raman instrumentation. The information provided by Brulin Corp. regarding the formulation of their products was of great help. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

REFERENCES

- (1) MIL-STD-1246C, "Product Cleanliness Levels and Contamination Control Program" – Institute of Environmental Sciences and Technology, 940 E. Northwest Highway, Mt. Prospect, IL 60056.
- (2) Y. Tito Sasaki, *J. Vac. Sci. Technol. A*, 9 (1991) 2025.
- (3) R.A. Rosenberg, M.W. McDowell, J.R. Noonan, *J. Vac. Sci. Technol. A*, 12 (1994) 1755.
- (4) C.L. Foerster, C. Lanni, R. Lee, G. Mitchell, W. Quade, *J. Vac. Sci. Technol. A*, 15 (1997) 731.
- (5) C. Benvenuti, G. Canil, P. Collin, R. Cosso, J. Guirin, S. Ilie, D. Latorre, K.S. Neil, *Vacuum*, 53 (1999) 317.
- (6) T. Shen and M. Fischer, "The Cleaning of Wrought Aluminum Alloy 6061-T6", LLNL report dated June 29, 2001, UCRL-ID-145445.
- (7) T. Shen, "The Cleaning of OAB Universal Covers- an Origin of Smut in Aluminum Alloys," LLNL report dated June 2, 2002, UCRL-ID-148327.
- (8) T. Shen, "The Gross Cleaning of Aluminum Alloys – The Effect of Caustic Etch on Smut Formation", LLNL report dated August 30, 2002, UCRL-MI-149969.
- (9) D.A. Jones, *Principles and Prevention of Corrosion*, Macmillan Publishing Co, New York, 1995.
- (10) J.R. Davis, Ed., *Corrosion of Aluminum and Aluminum Alloys*, ASM Intl., 1999.
- (11) C.E. Moffitt, D.M. Wieliczka, H.K. Yasuda, *Surf. Coat. Technol.*, 137 (2001) 188.
- (12) J.W. Diggle, A.K. Vijh, Eds., *Oxides and Oxide Films*, Marcel Dekker, Inc., 1976.
- (13) J. Rouquerol, J. Fraissard, J. Elston, B. Imelik, *J. Chim. Phys.*, 63 (1966) 607.
- (14) K. Kneipp, H. Kneipp, I. Itzkan, R.R. Dasari, M. S. Field, *Chem. Rev.*, 99 (1999) 2957.
- (15) A.M. Ahern, P.R. Schwartz, L. A. Shaffer, *Appl. Spectr.*, 46 (1992) 1412.
- (16) T. Schram, J. DeLaet, H. Terryn, *J. Electrochem. Soc.*, 145 (1998) 2733.
- (17) M. Rokita, M. Handke, W. Mozgawa, *J. Mol. Struct.*, 555 (2000) 351.

TABLES

Table 1. Vibrational mode assignments of observed Raman transitions.

Present work (cm^{-1})	Previously assigned modes (cm^{-1})	Bond
617/644	626/630 ^a	AlO_6 (octahedral)
772	668/772/731 ^a	AlO_4 (tetrahedral)
815	834 ^a , 840 ^b	AlO_4
	928/934 ^a , 916 ^b	AlO - Al asymmetric stretch
965	960 ^a	Phosphate stretch
	1056/1068 ^a	Al O bending mode
1040	1055/1117 ^a	Phosphate
1163		
1290	1290 ^b	Aluminum oxide mode
	1382/1358 ^a	carbon
	1584/1582 ^a	carbon
1388	1360 ^a	H_2O coordinated to AlO_4
1452	1425 ^a	H_2O coordinated to AlO_6
1535		
1600	1611 ^a	H_2O coordinated to AlO_6
	1645 ^a	physisorbed H_2O

^afrom ref. 14

^bfrom ref. 15

Table 2. Zeta potentials measured for particles in either deionized water or detergent.

Particle Type	Pretreatment	Solution	ζ (mV)
AA6061	unetched	DI ^a	-71.86 \pm 4.25
High purity Al	unetched	DI ^a	-61.50 \pm 7.97
AA6061	unetched	detergent ^b	-51.43 \pm 4.30
High purity Al	unetched	detergent ^b	-60.74 \pm 5.10
AA6061	H ₃ PO ₄ etched	DI ^a	-79.26 \pm 1.65
High purity Al	H ₃ PO ₄ etched	DI ^a	-70.17 \pm 7.60
AA6061	H ₃ PO ₄ etched	detergent ^b	-41.99 \pm 7.10
High purity Al	H ₃ PO ₄ etched	detergent ^b	-46.98 \pm 4.96

^a pH adjusted to 10.6 with sodium disilicate

^b 5% Brulin™ 1990GD, pH= 10.6

FIGURE CAPTIONS

Figure 1. (A) SEM micrograph of an AA6061-T6 aluminum surface. (B) Same surface, after the phosphoric acid etch and detergent cleaning, exhibits smoother features, and less adsorbed particles.

Figure 2. (A) Photograph of aluminum coupon coated with silver in the middle portion for SERS measurements. (B) Close -up image of the surface of Sample 1, shows pitted and smooth surface areas, as well as grooves from machining.

Figure 3. SERS spectra acquired in pitted regions at the surfaces of Samples 1, 2 and 3.

Figure 4. (A) SERS difference spectra showing the spectrum acquired for Sample 1 subtracted from the spectra of Samples 2 and 3, all data acquired in pitted regions (difference spectra generated from data shown in Figure 3). (B) SERS difference spectra acquired in smooth surface regions.

Figure 5. Averaged zeta potential measurements of pure aluminum and AA6061 particles with error bars.

FIGURES

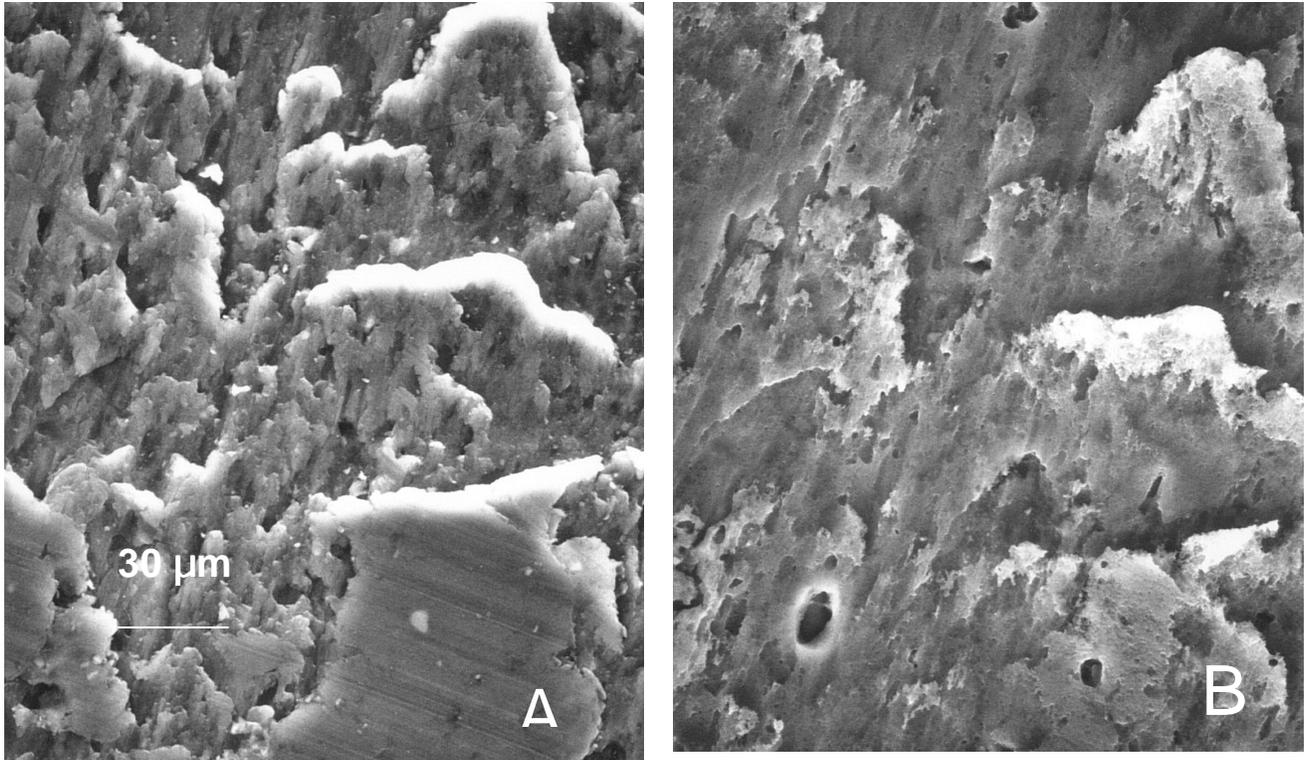


Figure 1A, 1B

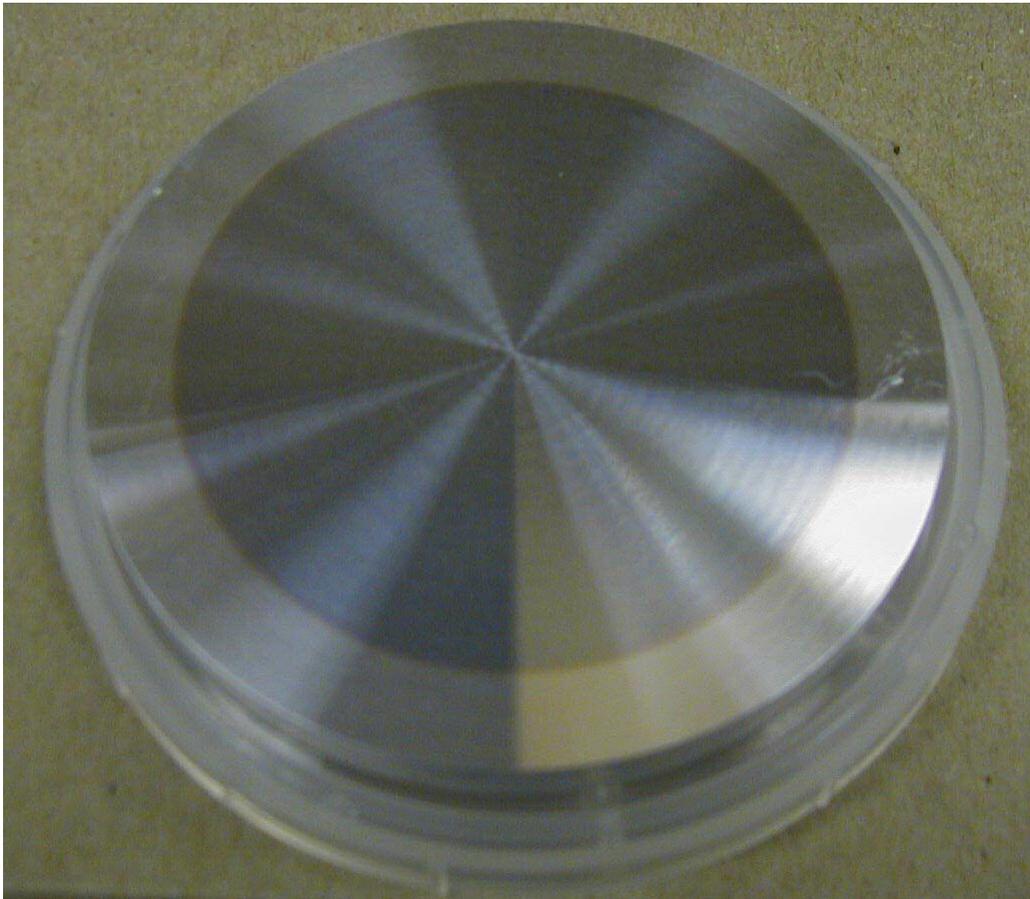


Figure 2A

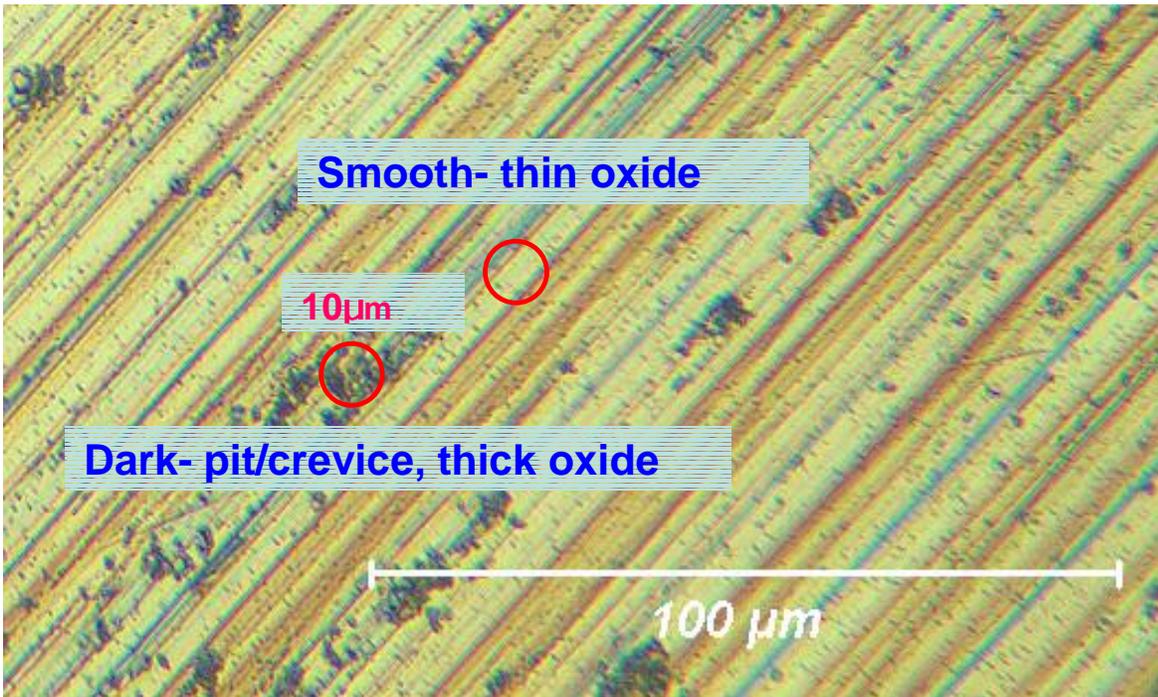


Figure 2B

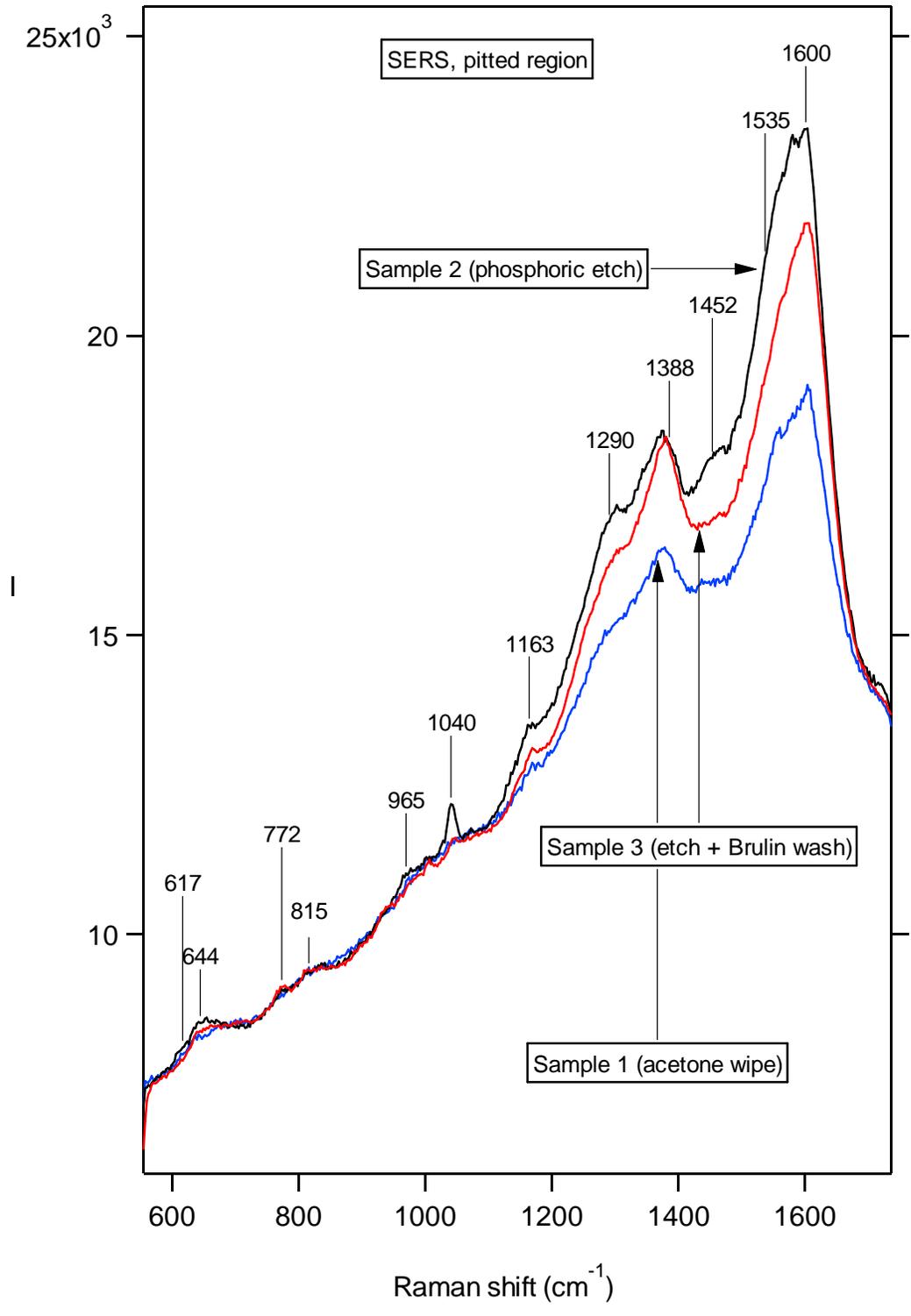
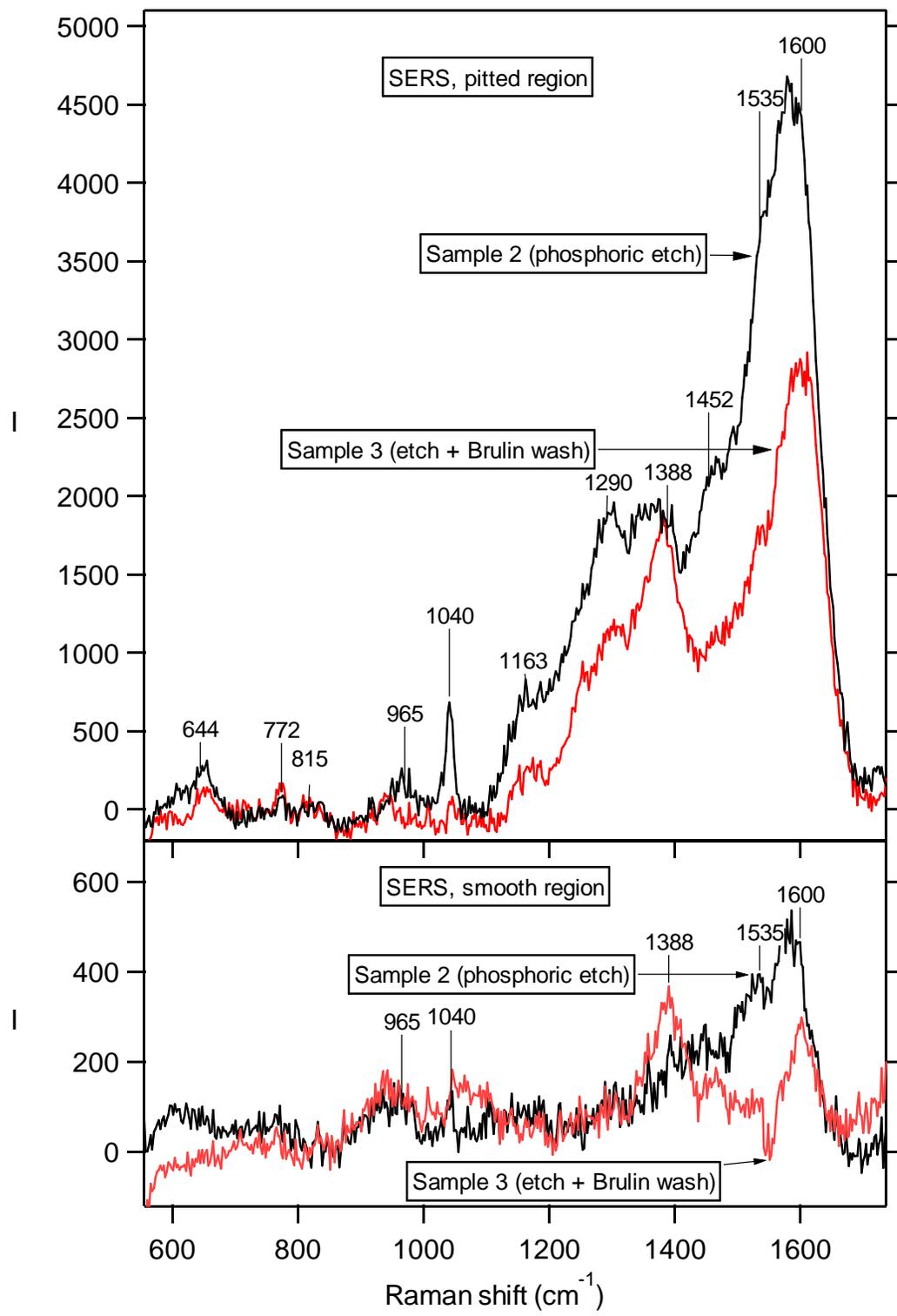


Figure 3



Figures 4A, 4B

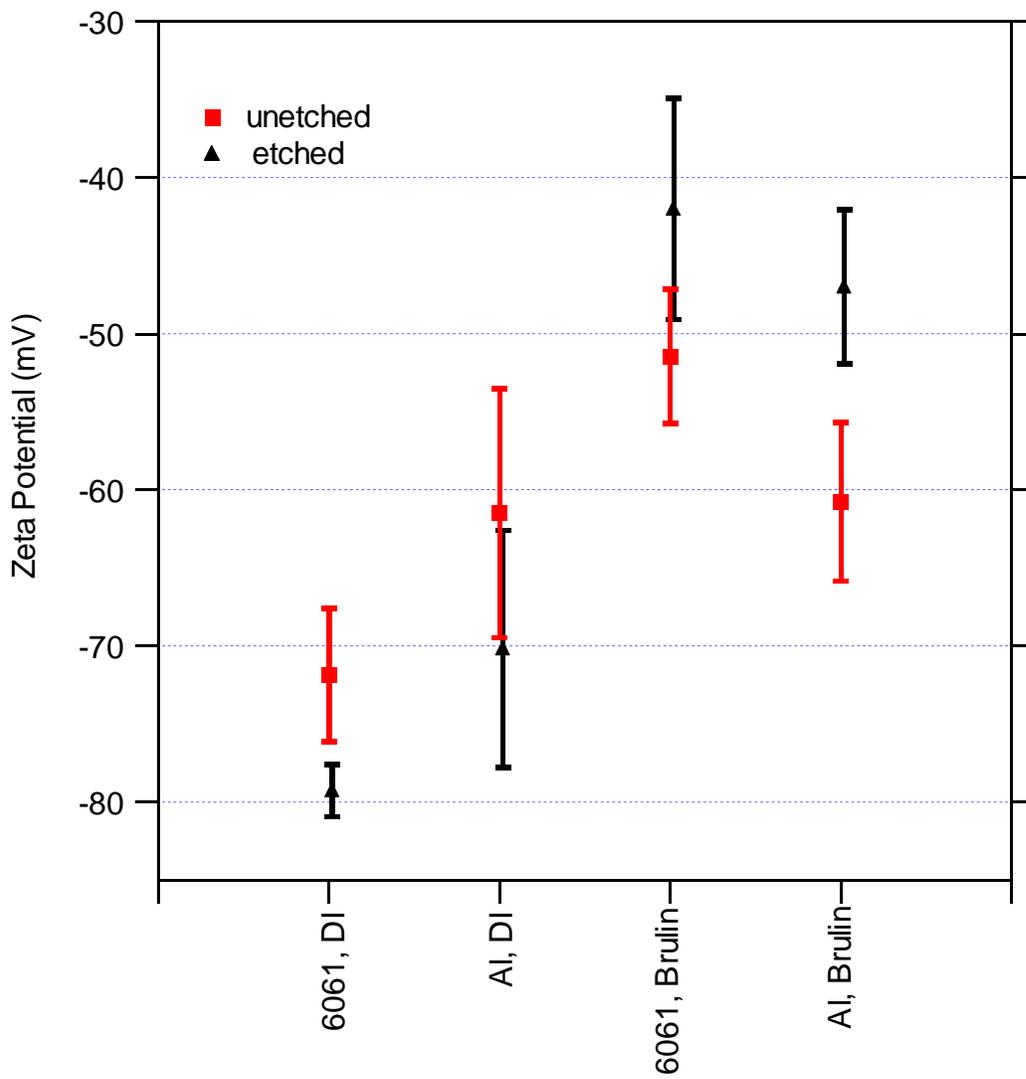


Figure 5